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SECOND SEMI-ANNUAL TECHNICAL REPORT
Report Date: January 10, 1962
July 10, 1961 to January 10, 1962

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Placed By:
U. S. Army Signal Research & Development Laboratories, Fort Monmouth, New Jersey

INVESTIGATION OF INTEGRALLY COMPOSED VARIABLE ENERGY GAP PHOTOVOLTAIC SOLAR ENERGY CONVERTER

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SECOND SEMIANNUAL TECHNICAL REPORT

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"INVESTIGATION OF INTEGRALLY COMPOSED VARIABLE ENERGY GAP PHOTOVOLTAIC SOLAR ENERGY CONVERTER"

ARPA Order Number 80-61

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Report Prepared By:

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and

W. E. Medcalf

The Eagle-Picher Company
Research Laboratories,
Miami, Oklahoma.

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I. PURPOSE

The general objective of this work is to fabricate and study an integrally composed variable energy gap solar cell and determine the feasibility of improving the photovoltaic properties of solar cells through the use of the variable gap principle. Special emphasis is placed on the improvement of efficiency, and the photovoltaic performance at temperatures above 25°C.

The variable gap cell under study is fabricated from two III-V compounds - Gallium Arsenide and Gallium Phosphide - in which the cell surface is composed principally of gallium phosphide forming a "window" of higher band gap energy than the gallium arsenide portion of the cell. A specific objective is to determine the feasibility of such a window as a means of achieving higher collection efficiency and lower sheet resistance.

The principle method of producing the variable band gap window is by solid state diffusion. The epitaxial growth method is included for study, although not investigated, as yet.

II. ABSTRACT

Gallium phosphide as a discrete phase has been produced by solid state diffusion of phosphorus into gallium arsenide. High concentrations of gallium phosphide, of the order of 90 percent, have been determined by x-ray analysis. Depths of 50 microns have been obtained.

Some knowledge of the conversion process has been obtained, allowing postulation of a step-type conversion mechanism, which is part of this report.

Tentative data indicates a non-linear diffusion-conversion rate, with rapid rates initially and very slow end rates for a given time of diffusion.

The diffusion rate or constant for zinc in gallium phosphide surfaces is observed to be significantly higher than in gallium arsenide by at least an order of magnitude, perhaps two or three orders of magnitude.

Two general species or categories have been selected as bracketing the various possible depths, concentrations, and gradients of variable gap cells. They represent very thin gallium phosphide surfaces, (1 to 2 microns deep), and deep (10 microns) layers. They

are found to exhibit quite dissimilar characteristics, especially in spectral response.

Efficiencies equal to single gap structure have been attained in the shallow species mentioned above. Indications of improved high temperature performance for this type cell have been found.

Spectral response data supports the principle of the high band gap "window" effect in the deep species.

An electro-etch-stain technique produces excellent definition of p-n junctions and gallium phosphide layers without destruction of the cell.

III. PUBLICATIONS, CONFERENCES, & REPORTS

Conferences.

A conference was held at Eagle-Picher Research Laboratories, Miami, Oklahoma, on July 25 and 26th., with Mr. Laurence Schwartz, of Evans Laboratories, and Messrs. W. E. Medcalf and Louis E. Stone, of this laboratory. The subject of the conference was the direction and emphasis of projected work, and the current progress of the investigation. Current state of progress specimen cells were delivered to Mr. Schwartz at this meeting.

A second conference was held on December 5, 1961, at Evans Laboratories with Messrs. Wm Cherry, L. Schwartz, and J. Mandelkorn, of Evans Laboratories, and Messrs. W.E. Medcalf and Louis E. Stone of Eagle-Picher Company. The purpose of the conference was again the current progress and direction of the investigation. Another group of specimen cells was delivered, and visual microscopic examination of other specimens was demonstrated. Both the aforementioned conferences were useful and very much worthwhile.

Reports:

Monthly Letter-Type reports have been submitted on or before the 4th. day of each month as per contractual agreement.

Publications:

A brief article, entitled "Conversion of Gallium Arsenide to Gallium Phosphide by Solid State Diffusion" has been submitted as a Letter to the Editor, Journal of Applied Physics, for publication.

IV. FACTUAL DATA

A. Introduction.

The theoretical basis for the research performed under this contract has been discussed in detail in previous reports[1]. Briefly the gallium arsenide-gallium phosphide cell would have a surface composed principally of gallium phosphide, diminishing in concentration with increasing depth. The higher energy gap layer would allow transmission of lower energy photons to a depth nearer the junction, improving collection and hence efficiency. The greater depth, when diffused with zinc as a p-type dopant, would reduce sheet resistance also. The higher band gap material would theoretically show improved high temperature characteristics. Emphasis was placed on the demonstration of such effects, including the "window effect" of the gallium phosphide layer. Inherent in the stated purpose is the study of the diffusion-conversion process to accomplish the variable gap structure, and derive controls for such processes and techniques which are required.

B. Approach to the Problem:

The approach to the problem includes the following:

1. Study of gallium arsenide crystals to obtain and improve starting materials.

2. Study of the diffusion-conversion process to accomplish the desired variable gap structure. This necessarily encompasses knowledge and control of the conversion mechanism to obtain discrete phase gallium phosphide rather than interstitially diffused phosphorus. It also implies determination of the optimum thickness and concentration of the gallium phosphide layer.

3. Study of the fabrication of variable gap cells, of the desired structure, and of single gap cells as a reference for comparison. This encompasses the following:

   (a). Techniques of forming p-n junctions in both types of cells, with emphasis in control of depth, density of dopant, and homogeneity of the diffused layer.

   (b). Identification and measurement of the gallium phosphide layer.

   (c). Identification and measurement of the depth of the p-n junction.

   (d). Electroding and contacting both type cells to obtain ohmic, low resistance contacts stable to temperatures of about 200°C.

4. Evaluation of Cells.

   The evaluation of cells is of prime importance. Routine analysis include the following:

   (a). V_{oc}, I_{sc}, and conversion efficiency.

   (b). Spectral response.

   (c). Diode characteristics.

   (d). Temperature coefficients of V_{oc}, I_{sc}, Eff_{mp}.

   Other parameters considered significant include:

   (a). Carrier concentration

   (b). Sheet resistance

   (c). Contact resistance

5. Evaluation of Starting Material.

   It is considered important to establish the effect of the following material characteristics on cell performance:

   (a). Resistivity

   (b). Mobility

   (c). Minority carrier lifetime

   (d). Crystal orientation

   (e). Gallium or arsenic face of the crystal.

C. Phosphorus Diffusion.

A major effort has been made during this work period to determine and clarify the mechanism involved in the conversion of gallium arsenide to gallium phosphide by solid state diffusion. This effort was required because of two prime factors: (a) The effect of varying phosphorus diffusion schedules was observed to change the photovoltaic parameters significantly, and (b) published reports[2] cast some doubt on the validity of our x-ray identification of discrete gallium phosphide present.

The DeBye-Scherrer powder diffraction technique has been widely used for the desired determination. Disadvantages of mechanical removal of such a thin layer from the surface of a cell was overcome by including prepared known size powder specimens in the ampoule during diffusion as already reported[3]. Full data on a series of such determinations follow in Table I.

TABLE I

Composition of Phosphorus Diffused Gallium Arsenide Powder, Based on X-Ray Studies.

Sample	M6108 BE	M6108 BF	M6108 BG	M6108 BH
Preparation:				
Time,	2 Hours	20 Hours	50 Hours	50 Hours
Temp. °C,	800°C	800°C	800°C	900°C
Pressure,	15 Atm.	15 Atm.	15 Atm.	20 Atm.
Gallium Phosphide Content of -				
Arsenic Rich Phase,	4.2%	38.6%	N.D.	1.5%
Phosphide " "	98.0%	99.5%	86.1%	93.1%
Strongest Intermediate Solid Solution Phase,	49.8%	86.1%	N.D.	N.D.
Gallium Phosphide Composition Calculated of all phases,	50.8%	81.4%	85.0%	88.5%

Figure 1 illustrates the appearance and color change in the above series of powder specimens. There is quite good correlation between the color changes and the gallium phosphide content as determined by x-ray.

Figure 1. Color Change of Phosphorus Diffused Gallium Arsenide Powder as a Function of Diffusion Schedules.

Some discussion of the x-ray data is in order. The pattern of the more heavily diffused specimens were normal, well defined, and sharp. The pattern of the more lightly diffused specimen, M6108 BE, however, was that of two major phases of similar crystal structure with edge lengths differing by only about 0.1 A°. This results in a repeated pattern of lines, as would be expected. However, the space between the lines of the two patterns are filled with sharply defined lines, or striae, which are very distinct on the larger spacings (low theta angles). These intermediate lines come from well defined crystalline phases, evidently of

compositions intermediate between the two major phases that are the end members of the solid solution system present in the sample.

The line structuresare also of interest. The line of the pattern from the arsenic rich end member is very grainy, indicating a particle size at least an order, perhaps 2 or 3 orders, of magnitude greater than that of the smooth fine-grain line from the phosphorus rich end member.

With gallium arsenide as the starting material, the phosphorus diffusion-conversion mechanism may be postulated as taking place into the surface by a series of discrete steps. Each step would comprise a thin zone and within that zone it's composition would be uniform. At the stage which M6108 BE was prepared at least five such zones can be identified. Each zone represents an equilibrium condition, since it has a crystalline structure in keeping with it's composition. Since these zones are thin, their diffraction patterns are fine-grained. The central "kernel" of each powder particle of gallium arsenide may have a diameter many times thicker than the thickness of each separate zone. Confirmation of the presence of such strias was obtained photographically. Figure 2 illustrates such strias in specimen M6108 AA, which was phosphorus diffused at 800°C - 15 atmospheres, 7 1/2 hours. In the cross section view, the white area is the polished gallium arsenide surface. The gallium phosphide layer lies between 3.1 and 3.2 scale divisions. The lower irregular line at 3.2 represents the innermost boundary of gallium phosphide, as defined by electro-etch staining (which will be described later). The strias are visible, and were very well defined under direct microscopy.

Figure 2. Cross Section View of Variable Gap Wafers Showing Striae.

Note was made that in the heavily diffused members of the series, M6108 BC and M6108 BH, the presence of intermediate phases were not found. The implication is that conversion occurred all the way to the center of the 5-micron radius powder particles. This is in agreement with microscopic evidence of wafers diffused simultaneously with the powder specimens in which a layer of gallium phosphide 10 to 15 microns thick was observed and photographed.

Figure 3 illustretes wefer specimen M6108 BH, in cross-section view after etching heavily to define the gellium phosphide leyer.

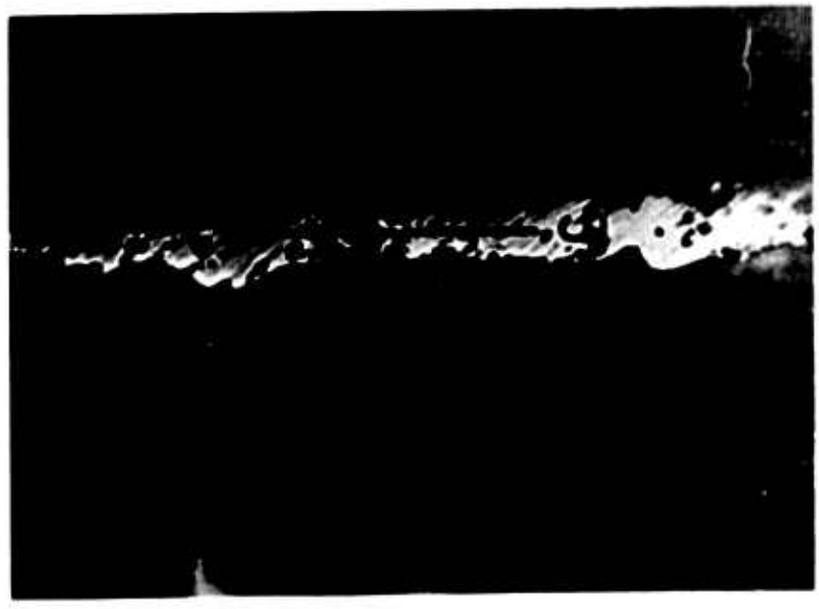


Figure 3. Cross Section View of M6108 BH Wafer Showing 10-Micron Gellium Phosphide Layer. (500x).

Some effort was made to define the diffusion-conversion rate. Teble II indicates measurements made of varieble gap structures of different diffusion schedules.

TABLE II

Measured Depths of Gallium Phosphide Layers

Identity Numbers	Phosphorus Temp. °C.	Diffusion Pressure-Atm.	Time (Hours)	Depth (Microns)	Percent Concentration By X-Ray
M6108 BE	800°C	15 Atmos.	2 Hrs.	-------?	50.8%
M6108 AA	800°C	15 "	7 1/2 Hrs.	About 2	73.0
M6108 BF	800°C	15 "	20 Hrs.	2	81.4
M6108 BG	800°C	15 "	50 Hrs.	2 or 3	85.0
M6108 BH	900°C	20 "	50 Hrs.	10	88.0
M6111 BE	950°C	20 "	170 Hrs.	30	> 90.0
M6111 BF	950°C	20 "	340 Hrs.	50	> 90.0

The data in this table must be interpreted in the light of the following factors:

1. The concentration of gallium phosphide appears to affect the etch resistance of a layer; M6108 BE corresponds to x-ray date indicating 50 percent concentration; it appears to be attacked by the etchant. Etching did not clearly define a layer, although other evidence strongly indicated such was present.

2. The figures listed for M6111 BE and M6111 BF are for the maximum depth. Each wafer had a highly polished face, and an unpolished face. The polished face indicated 20 and 40 microns, respectively, in depth. The unpolished face indicated rather large crystalline protuberences grown out of the face, apparently the result of nucleated epitaxial growth. This side had the deeper layer. It is not known which (arsenide or gallium) lattice face this might represent.

3. The number of specimens involved is not statistically large.

4. The conversion process is known to be both pressure and temperature sensitive.

The data does support the following tentative conclusions:

1. The initial rate of diffusion-conversion at pressures of the order of 15 atmospheres, is very rapid, exceeding the diffusion rate of phosphorus at atmospheric pressures, or less, by several orders of magnitude.

2. The initial rapid rate decays more rapidly than the usual error function associated with diffusion processes.

3. The overall diffusion is very non-linear and does not conform to the Boltzmann model.

4. The overall depth and concentration appears most dependent upon temperature, secondarily upon pressure, and thirdly upon time, in the pressure region 15 to 20 atmospheres.

It is interesting to note that gallium phosphide crystals were formed at one end of the ampoules during the longer time runs. The ampoules are prepared with phosphorus at one end, specimens in the center, other end sealed under vacuum. Cooling is done slowly, with the sealed end protruding into a cooled zone to condense the phosphorus and prevent deposits of elemental phosphorus on the wafers. At the opposite end of the ampoules, pure gallium phosphide crystals were observed, larger in size in the longer time ampoule. This may offer a different technique of growing gallium phosphide crystals from the vapor phase, if the ampoule contained elemental gallium instead of gallium arsenide wafers.

With the objective of preparing shallow layers of very high gallium phosphide concentration, two tentative experiments were made of phosphorus diffusion at slightly more than 30 atmospheres pressure, 800°C for two hours. Powder specimens were included. X-ray patterns were poorly defined and judged not usable for calculation. Cells were observed to have a glass-like film coating. Zinc diffusion resulted in a very thin (estimated of the order of .2 micron) photogenerating surface. In the second experiment the same film was noted and removed prior to zinc diffusion with concentrated HF acid. Cells fabricated thus were poor, and lacked the usual varieble gap characteristics. It is possible

that this order of pressure exceeds the dissassociation pressure of gallium arsenide and inhibits the conversion process. An alternative explanation contemplates the rapid formation of an SiO_2 film to produce the same result. In the interest of expediency, it was decided to limit, at present, the fabrication to 20 atmospheres pressure.

The many possible depths of gallium phosphide layers, further complexed by concentration variables, required limitation if the investigation was to adhere to it's main objectives. Therefore, it was decided to use two "species" of variable gap structures, i.e., one with shallow, minimal gallium phosphide layer depth as produced by phosphorus diffusion schedules of 800°C - 15 atmospheres, 2 to 10 hours, and the other of fairly deep gallium phosphide structure, as produced by schedules of the order of 900°C - 20 atmospheres, 2 to 50 hours. These two species are considered to bracket the desired structure for the variable gap cell.

D. Zinc Diffusion.

Zinc diffusion as previously reported[3] has been done in tube furnaces, in ambient hydrogen atmosphere. The specimen and dopant are placed in a clean quartz boat, which is reteined in the tube external to the furnace during outgassing and heat up. Temperature is measured by a quartz enclosed thermocouple inserted in the tube to the center of the hot zone. When the desired stabilized temperature has been attained, the boat is moved to the center of the hot zone for the desired length of time. Quick cooling is obtained by removing, the entire tube from the furnace,

boat moved back to it's former position and the entire tube cooled by evaporation. The hydrogen atmosphere is maintained until cooled to room temperature. Argon gas is used for purging.

Initial fabrication and testing of single gap cells indicated diffusion schedules of about 600°C for 5 to 6 minutes produced satisfactory junctions about 1-micron deep. Spectral response curves corroborated this order of depth, indicating fairly broad response in the blue region, peaking in the .8-micron wavelength region. Junction depth measurements on cells with fairly deep gallium phosphide layers (10-Microns) repeatedly indicated the junction to be at the bottom of such layers. The indication of a more rapid diffusion rate of zinc in gallium phosphide supports the available information in the literature[4].

Table III indicates typical 4-probe measurements of both single gap and variable gap cells at appropriate points of fabrication. All cells had similar polished surfaces, and similar diffusion techniques.

TABLE III

Typical 4-Probe Data of Single Gap and Variable Gap Cells.

Type Cell	Number of Cells	Initial Surface 4-Probe ohms/sq.	4-Probe ohms/sq. After Phos. Dif.	4-Probe ohms-sq. Zinc Dif.	Zinc Diffusion Schedule
Variable Gap,	4	1000 - 1700	6000	5.	650°C-10 Min.
Single Gap,	3	900 - 1200	----	3.5	" " "
Variable Gap,	8	900 - 1000	7200	7.5	600°C- 5 Min.
Single Gap,	4	700 - 900	----	7.5	" " "

The table indicates typical increased surface resistance after phosphorus diffusion and approximately equal resistivities, and

therefore equal surface carrier concentrations, of both type cells after zinc diffusion.

The indication of a more rapid diffusion rate of zinc in gallium phosphide layers suggested an experimental comparison. Two wafers of similar material, one having a gallium phosphide layer 10 to 12 microns thick, were diffused simultaneously with zinc at 850°C for 10 minutes. As expected, this produced a p-n junction 10-microns deep in the plain wafer, as determined by direct microscopic measurement and by etch-weight loss methods. An electro-etch stain technique, to be described later, produced clear definition of the junction. Similar measurement of the variable gap cell by both cross-section and angle lapped methods is illustrated in Figure 4, and clearly indicated the junction to be about 20-microns deep. Positive identity of the junction was proved by micro-manipulator probing along the surfaces under 100x magnification, using the vertical microscopic illuminator for excitation. The zinc penetration thus was 10-microns in the plain wafer, and in the variable gap structure was 10 to 12 microns of gallium phosphide plus about 8-microns of gallium arsenide. The indication thus is that zinc penetrated the 10 to 12 micron gallium phosphide layer as easily as 0 to 2-microns of gallium arsenide.

Figure 4. Cross Section View of P-N Junction in Veriable Gap Cell. (500x).

The indicetion, therefore, is at least an order of magnitude faster zinc diffusion in the gallium phosphide leyer than in gallium arsenide, perhaps two or three orders. This prompted an effort to reduce the diffusion schedules to produce the junction within the gallium phosphide layers. It wes considered edviseble to hold the time of diffusion to no less than 10 minutes initislly. A series of diffusions were carried out with temperetures decreasing from 600°C in 25°C steps. Each group consisted of one lightly phosphorus diffused wafer, one heavily diffused wefer, and one or more plein gallium arsenide wefers. Unfortunetely, e materiels veriable wes introduced, as the wefers were from different starting materiels. The results of this series are, as yet incomplete. The single gap cells indicate a progressively shallower junction, with Eff_{mp} good at 550 to 500°C.

The phosphorus diffused cells indicate improving Eff_{mp} at 525°C. Further discussion of this study is made under "Evaluation".

E. Fabrication.

The general order of fabrication steps has been reported in detail in the preceding report[3]. Essentially the same techniques are currently in use, with somewhat more attention paid to clean surfaces and ohmicity.

F. Contacting.

Electrically plated nickel contacts are used to contact the n-type bulk material and sputtered platinum contacts to the p-type surface. As reported previously[3] some non-ohmicity was experienced with high resistivity material, as well as non-uniform plating. The non-uniform plating was found to be a material characteristic, and the poor ohmicity traced to the nickel contact. Heat treating of both contacts, inherent in the solder-coating step, produced good ohmic contacts. Hence, solder coating is now routine.

G. Evaluation.

1. General.

The evaluation of solar cells includes routinely the following procedure:

Photo-parameters, V_{oc}, I_{sc}, Eff_{mp} are measured under 100-milliwatts of light from a Type RFL-2 bulb. Incident light is filtered through 1-inch layer of water in a suitable pyrex container and measured with an Eppley pyrheliometer. Short circuit current is measured as a voltage drop across a 1-ohm load resistor.

Diode characteristics are measured, using a Techtronix Oscilloscope and curve tracer adapter. When desired, direct current plots are made.

Spectral response data are obtained using a Bausch & Lomb Spectro-Photometer of the grating type.

2. Junction Depth and Carrier Concentration.

Junction depth measurements have been greatly facilitated by a technique developed early in this work period. The technique allows non-destructive determination of p-n junction and delineates the gallium phosphide layer simultaneously, using the finished cell. The cell is mounted edge-wise in the groove, sawed in a porcelain block, with one edge protruding slightly. Wire electrodes are brought out the ends of the groove. The protruding edge is lapped and polished. Figure 5 illustrates the mounted, polished cell. A potential is applied across the cell, positive to "p" side, negative to "n" side, sufficient to produce about 5 to 10 milliamperes forward current.

Figure 5. Edge-Mounted Polished Cell Prepared for Electro-Etch-Staining.

A few drops of NH_4Cl of about 4-molar concentration are placed on the exposed edge of the cell for 15 to 30 minutes. The cell is then rinsed carefully and blotted dry. Under magnification, "p" areas are observed stained, "n" areas unstained, with the junction sharply defined by a dark line. Variable gap cells also are found to have the gallium phosphide layers well defined. The same technique is applicable to angle lapped cells. Figure 6 illustrates the junction in a single gap cell, angle lapped, under 500x magnification.

Figure 6. P-N Junction in Angle Lapped Single Gap Cell After Electro-Etch-Stain. (500x).

Where no junction is present, the gallium phosphide is also easily and well defined by etching in a solution of 1-$KOH_{(6n)}$ 2-H_2O_2 (30%) 5-H_2O for 15 to 30 seconds. Using either method, direct microscopic measurement to about 1-micron may be made at 500x. Shallower depths will require higher magnification and resolution.

Fairly good correlation has been observed between diffusion schedules and the time required to etch single gap cells to zero short circuit current. The solution used is 1-2-5 KOH(6 normal) H_2O_2 (30%) H_2O, at room temperature. The general pattern is described in detail in a previous report(5). Briefly, the I_{sc} shows a rapid increase as the junction is approached, decays quickly to zero as it is dissolved.

Approximate depths may be estimated by time, and as indicated in Table IV, the junctions formed at the lower temperatures are extremely shallow.

TABLE IV

Etch Time to Zero I_{sc} as a Function of Low Temperature Zinc Diffusion for Single Gap Cells.

Diffusion Schedule	Approx. Etch Time to Zero I_{sc}	Est. Junction Depth	Remarks
600°C-10 Minutes,	15 Seconds,	1.0-1.5 Microns,	Rise I_{sc} to peak at 6 seconds
575°C-10 Minutes,	12 Seconds,	.8 - 1.2 "	Rise to peak I_{sc} at 4 seconds.
550°C-10 Minutes,	8 Seconds,	.6 - 1.0 "	Slight rise, drop at 4 seconds.
525°C-10 Minutes,	6 Seconds,	.5 - .8 "	No rise, drop at 2 seconds.
500°C-10 Minutes,	4 Seconds,	Less than .5 "	No rise; drop 50% in 2 seconds.
475°C-10 Minutes,	2 Seconds,	About .1 "	

Carrier concentrations have been determined by 4-probe measurements. A disadvantage has been observed in cells with shallow junctions in that mechanical puncturing of the layers occure frequently, ruining the cell. Consequently, carrier concentration data on the most recent low temperature zinc diffusion work is not complete. Tentative data indicate that carrier concentration drops rapidly below 550°C diffusion temperatures. Approximately 10^{19} carriers/cm^3 are obtained in either type cell above this temperature.

3. Efficiencies.

Typical photo parameters of single gap, shallow gallium phosphide and deep gallium phosphide variable gap cells are given in Table V. Data were obtained under 100 milliwatt light input through a 1-inch H_2O filter.

TABLE V

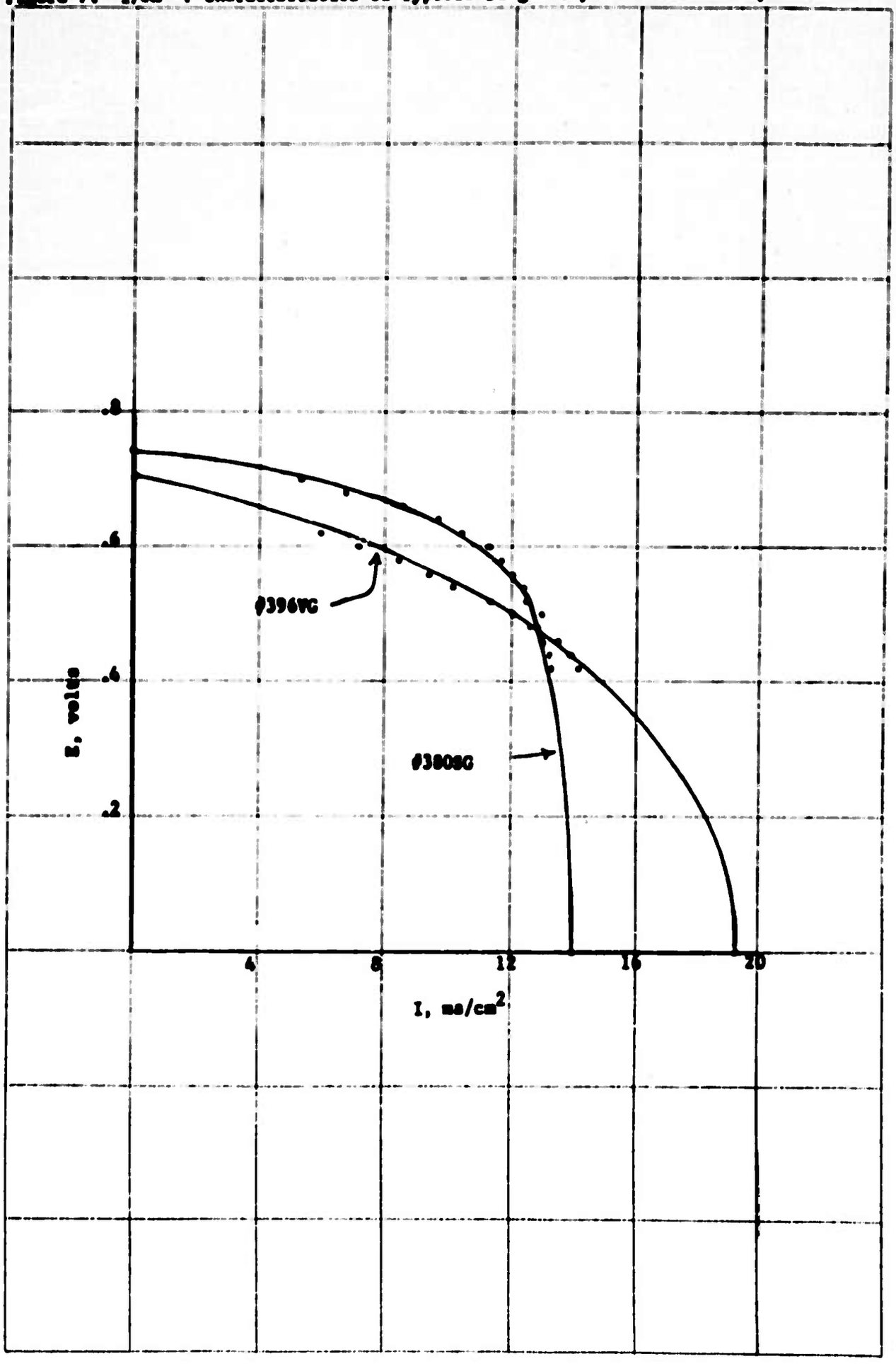
Typical Photo Parameters of Single Gap, Shallow Gallium Phosphide and Deep Gallium Phosphide Variable Gap Cells.

Type & No. of Cell	Phosphorus History	Zinc History	V_{oc}	I_{sc}/cm^2	Eff_{ap}	V_L
380 S.G.	- - - - - - - - -	600°C-5 Min.	.74	14.ma	6.8%	.60v
382 S. G.	- - - - - - - - -	600°C-4 Min.	.72	17. "	7.5%	.54v
403 S. G.	- - - - - - - - -	540°C-10 Min.	.70	14. "	6.15%	.50v
384 V. G.	800°C-15 Atm-3 Hrs.	600°C-4 Min.	.65	19. "	5.5%	.41v
396 V. G.	800°C-15 Atm-2 Hrs.	550°C-10 Min.	.72	16.5"	6.3%	.47v
405 V. G.	800°C-15 Atm-2 Hrs.	525°C-10 Min.	.68	17.4	6.1%	.48v
401 V. G.	900°C-20 Atm-50 Hrs.	550°C-10 Min.	.42	3.3 "	1.0%	.35v
402 V. G.	900°C-20 Atm-50 Hrs.	550°C-10 Min.	.65	2.5 "	1.0%	.44v

It is significant to state that two (#384 and #396) of the variable gap cells were large area cells, enhancing accuracy of measurements, and were of the same order of efficiency as the single gap cells. It is considered useless to speculate upon the low efficiencies of the deep gallium phosphide cells (#401 and #402) since so few of this type have been fabricated thus far. Some significant data has been obtained on this type, however, and is discussed subsequently.

The I-V characteristic can be informative in the realm of conversion efficiencies. Typical I-V plots for single gap and variable gap cells are given in Figure 7. Current is plotted per unit area, allowing valid comparison.

Figure 7. I/cm^2-V Characteristics of Typical Single Cap and Variable Cap Cells



The single gap cell characteristics require little comment. The plot is rectangular, and indicates little resistive effects. The plot of the variable gap cell does indicate some series resistance in the slope of the high current region. This is considered to be a composite effect of sheet resistance, and bulk resistance in the gallium phosphide layer, produced by the presence of interstitial phosphorus. A contributing factor may well be the high resistivity (.05 ohm-cm) starting material. The fairly good efficiency (6 percent) of this cell appears encouraging to further improvement.

4. Temperature Characteristics.

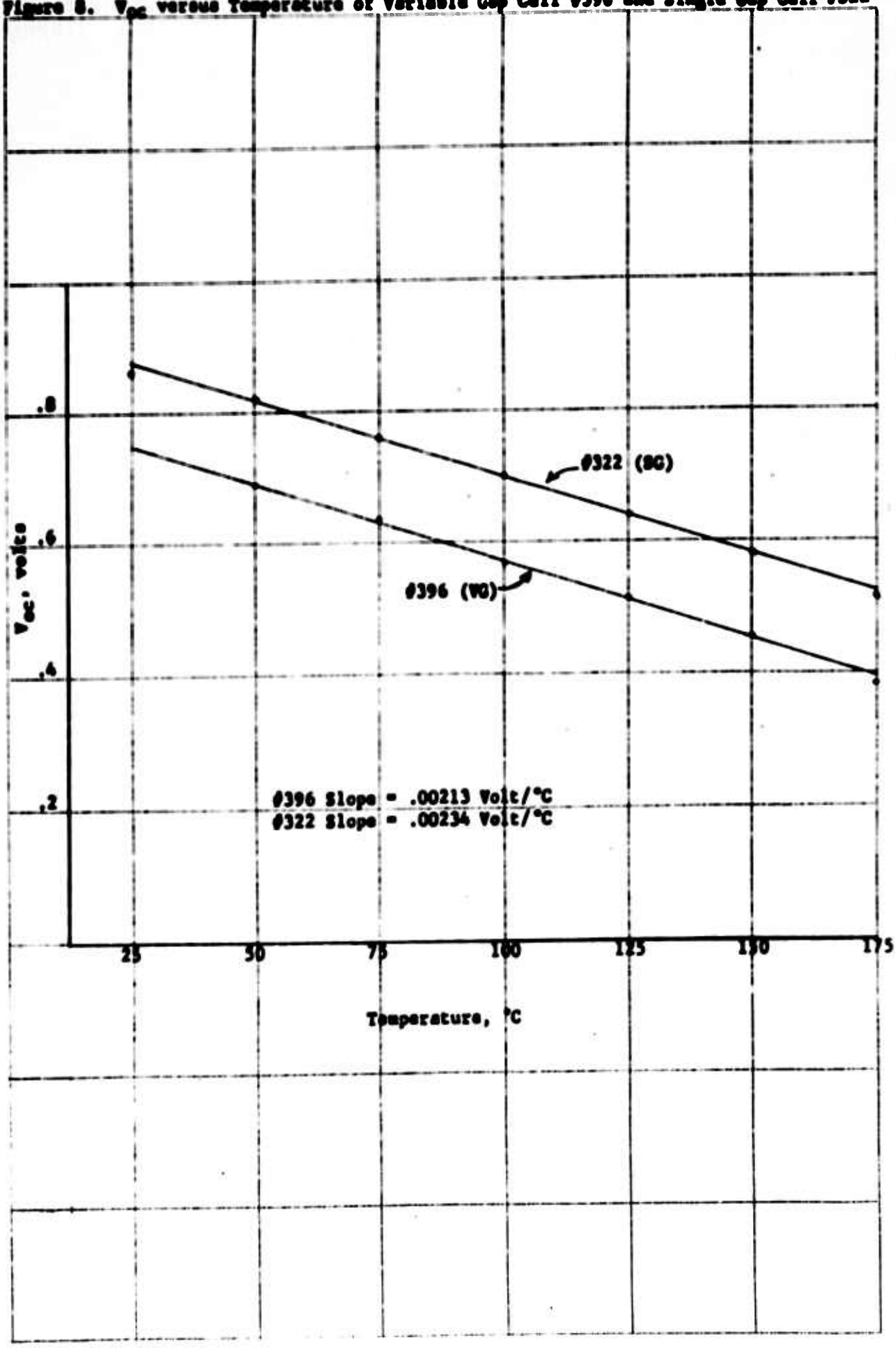
The technique for measuring V_{oc}, etc., versus temperature was reported and illustrated in detail in the previous report(3). The results of several such tests upon typical cells agree closely with tentative data given in that report, and are summarized as follows:

The drop in V_{oc} with increasing temperature give a straight line slope of .00234 + volts/°C for both our own single gap cells and cells fabricated elsewhere.

The drop in V_{oc} with increasing temperature of variable gap cells of the lightly diffused species is regularly less, .00210 v/°C average. Figure 8 is a typical plot of this factor. The I_{sc} versus temperature curves for variable gap cells usually show a more inclined rise than for single gap cells. It is considered this may be related to residual, interstitial, elemental phosphorus in the lattice, which is annealed out during the heating process in testing. Tentative heat treatment of cells in a hydrogen atmosphere appears to increase slightly initial I_{sc} and flatten the rise of I_{sc}. Further evaluation of this point is expected soon.

The drop in Eff_{mp} versus temperature of the lightly diffused species of variable gap cells is measurably less, but only by a small factor.

Figure 8. V_{oc} versus Temperature of Variable Gap Cell #396 and Single Gap Cell #322



5. Diode Characteristics.

Dark diode data is useful in assessing junction quality and resistive effects. Commonly, both variable gap and single gap cells exhibit good steep forward current slopes, indicating in excess of 60 milliamperes forward current at one volt. Some variable gap cells, although of good efficiency, reflect resistive effects in the forward current slope. Cell #396, variable gap, Eff_{mp} = 6 percent, is such a cell. Figure 9 illustrates it's diode characteristics. Also shown is Cell #394 (variable gap) having low forward resistance, and Cell #393 (single gap) for comparison. These three are typical of all cells.

6. Spectral Response.

Spectral response is regularly monitored in cells. The response of a series of single gap cells with junctions decreasing in depth show the expected increase in short wavelength response. Good correlation is noted between this blue response and diffusion schedules and junction depths. Figure 10 illustrates the progressive increase of response in the 400 to 600 millimicron region of a series of single gap cells.

It is of interest to note that the single gap cells, although having bored response, retain the high response into the 800 to 850 millimicron region. A characteristic of the shallow gallium phosphide variable gap cell is noted in the peak response occurring at about 700 millimicrons, dropping significantly in the 850 millimicron region. A dramatic difference is noted in deep gallium phosphide variable gap cells, with a pronounced peak, or peaks, occurring in the 400 to 600 millimicron region, and a sharply defined peak at 850 millimicrons.

Figure 11 illustrates typical response curves of the two types.

The peak observed in the short wavelength region is closely related to the band edge of gallium phosphide; that at 850 millimicrons to the band edge of gallium arsenide. This response is easily reproducible in the deep gallium phosphide cells, varying somewhat in amplitude. It is considered significant as a method of monitoring the contribution of current from the higher band gap material.

It is important to note that the response at 850 millimicrons supports strongly the theory of the high band gap "window" principle. This seems reasonable since the gallium phosphide layer is known to be in excess of 10 microns thick, the surface concentration is known to be predominantly gallium phosphide, and the junction is known to be at the bottom of the gallium phosphide layer. The markedly sharp peak at 850 millimicrons supports the conclusion that the "window" transmitted this order of wavelength without great attenuation or absorption.

Figure 9. Typical Dark Diode Curves of Single Gap and Variable Gap Cells

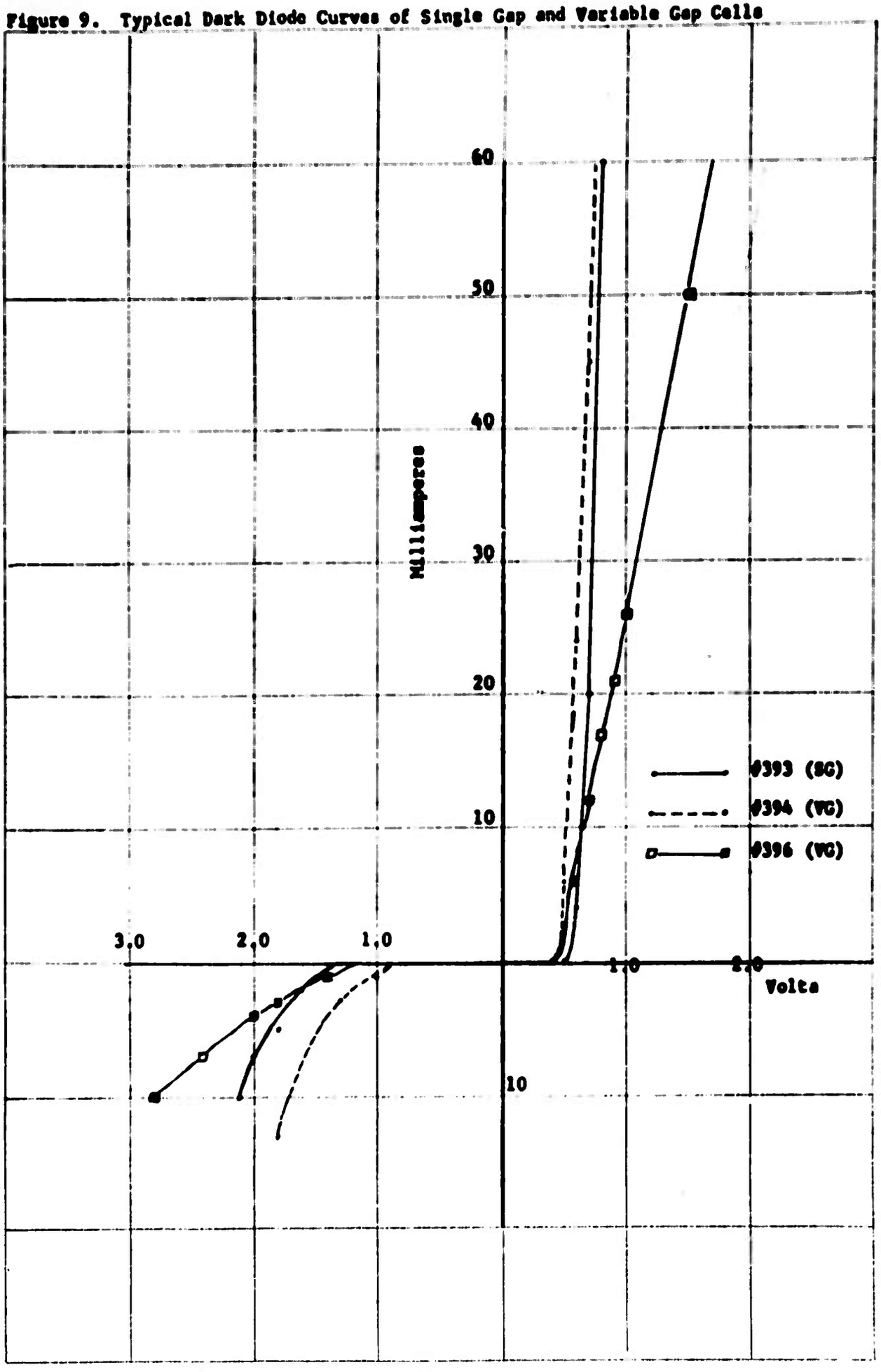


Figure 10. Spectral Response Compared to Zn Diffusion of Single Cap Cells

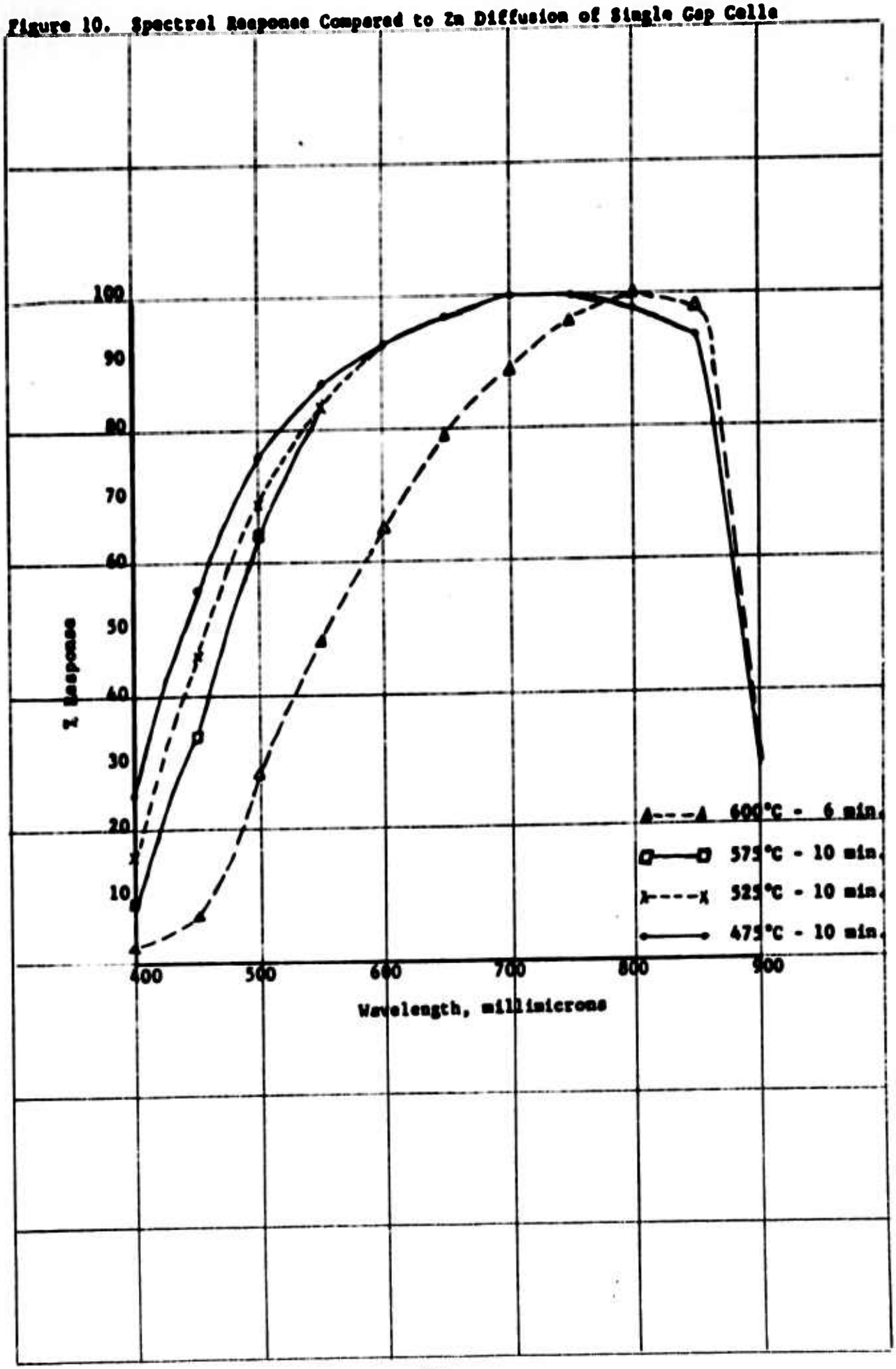
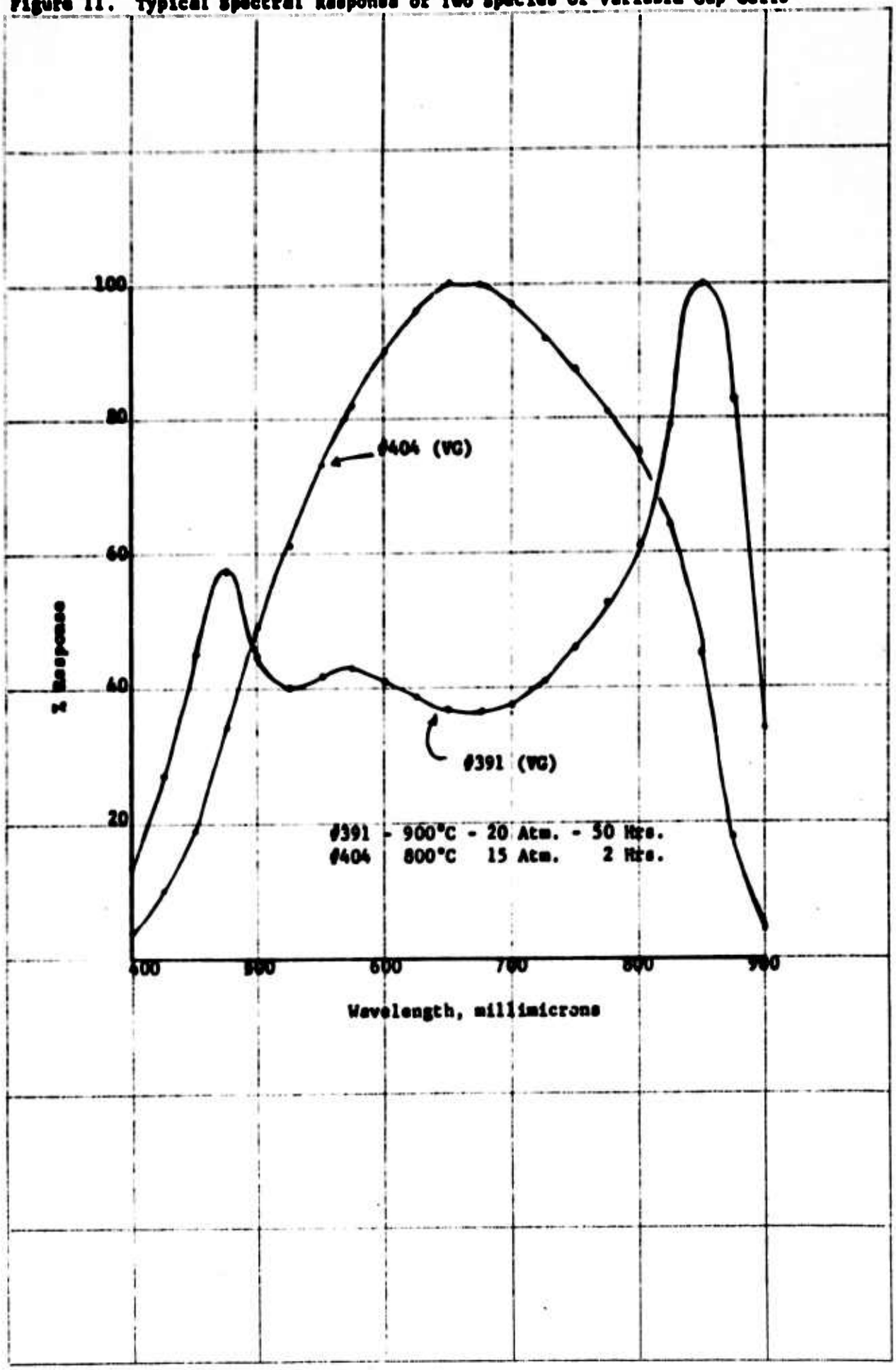


Figure 11. Typical Spectral Response of Two Species of Variable Gap Cells



V. CONCLUSIONS

It may safely be stated that the compound structure gallium phosphide-gallium arsenide with intermediate thin incremental transition regions is produced by solid state diffusion of phosphorus into gallium arsenide at phosphorus pressures in excess of 8 atmospheres.

The diffusion-conversion rate of gallium phosphide formation is pressure and temperature sensitive, is initially more rapid by orders of magnitude than classic phosphorus diffusion, and is extremely non-linear. Significant depth differences between the polished and unpolished side of the same wafer have been observed.

The diffusion rate of zinc into gallium phosphide-gallium arsenide alloys of high gallium phosphide content is significantly faster than in gallium arsenide, and is estimated as greater by one or two orders of magnitude. The "window" effect of the higher band gap layer is valid, and demonstrated by spectral response data included in this report.

Variable gap cells of one specie can be of at least equal efficiency as the conventional single gap cell, and it appears feasible to produce good efficiency in deeper gallium phosphide layers.

The technique of electro-etch-staining of variable gap or single gap cells provides a very good, non-destructive definition of the junction and gallium phosphide layers.

Variable gap cells of one specie exhibits a measurable, although small, advantage in high temperature performance. Further advantage appears likely with improved techniques, materials, and control.

The presence of, and contribution from, the higher band gap component in the variable gap cell is observed in spectral response data.

The contacting of gallium phosphide surfaces for low contact resistance, ohmicity, etc., is possible, although the present system of contacts may be improved, and will be in the normal course of the investigation.

No well defined relation has been observed between crystal orientation and efficiency as yet. This factor may be obscured by other variables.

VI. FUTURE STUDIES

It is considered that future studies should include the following:

(a). Pursuit of the deeper gallium phosphide species of cell, with the object of producing a cell combining good efficiency, improved high temperature performance and demonstrative short wavelength response in the 400 to 600 millimicron region related to the band edge of gallium phosphide. It is considered gallium phosphide depth of such a cell might be 2 to 5 microns.

(b). Studies of controls and technique of dopant diffusion aimed at producing the junction in the gallium phosphide layer or below it, rather than the latter only. This may prove especially important in the shallow gallium phosphide type of cell.

(c). The shallow species of cell should be tested, with less emphasis perhaps, pending better control of junction depth.

(d). Investigation, by supplying appropriate specimen cells to Signal Corps Personnel, of radiation resistance and similar characteristics. Tentative discussion and delivery of a specimen cell was made toward this end at a conference in December, 1961.

(e). Studies intended to evaluate the effect of annealing, under hydrogen, variable gap structures to eliminate any interstitial elemental phosphorus.

(f). Evaluation of the rate of increase of efficiency with increased light intensity. Some evidence has indicated an advantage of the variable gap cells in this report, which would be of importance in solar concentrator applications.

(g). Study and comparison of epitaxially grown gallium phosphide layers, in which no diffusion occurs, and the current solid state diffusion type of variable gap cell.

(h). Studies of a concurrent, cumulative nature which would provide data on -

Materials parameters relative to efficiency.
Crystal orientation with regard to gallium phosphide conversion rates and/or diffusion rates of zinc.

Optimum gallium phosphide concentration and depth for variable gap cells as related to efficiency.

Optimum position of p-n junction relative to efficiency.

VII. REFERENCES

(1). Final Technical Summary Report, Contract DA-36-039-SC-85246. The Eagle-Picher Company.

(2). Final Progress Report, November 21, 1960, Contract DA-36-039-SC-78164.

(3). First Semi-Annual Technical Report, July 10, 1961. Contract Nr. DA-36-039-SC-87408

(4). Gershenson, Frosch, Mikulyak - "Precipitation in Gallium Phosphide". Abs. of Electrochemical Society, May, 1961.

(5). Second Technical Summary Report, July 10, 1960. Contract DA-36-039-SC-85246.

VIII. PERSONNEL

Engineering Time Expended from July 10, 1961 to January 10,1962.

	HOURS
W. E. Medcalf, ...	200
Joseph E. Powderly,.	197
Louis E. Stone,.	968
George N. Webb,.	922
	2,287 Hours.

AD_____ Accession No._____

The Eagle-Picher Company, Chemical & Metals Division, Miami, Okla.
INVESTIGATION OF INTEGRALLY COMPOSED VARIABLE ENERGY GAP PHOTOVOLTAIC SOLAR ENERGY CONVERTER.
L. E. Stone and W. E. Medcalf
Second Semiannual Technical Report- July 10,1961 to Jan. 10,1962.
36 pp - Illus. - Graphs
Signal Corps Contract Nr. DA-36-039-SC-87408 Unclassified Report.

Gallium phosphide as a discrete phase has been produced in gallium arsenide;concentration of the order of 90 percent identified by x-ray analysis. Photographs of gallium phosphide layers defined by etching are included. Depths of 50 microns were obtained, and diffusion schedules given. A step-type conversion mechanism is postulated; evidence indicates a very non-linear conversion-diffusion rate which is temperature and pressure sensitive. The diffusion rate of zinc in gallium phosphide-gallium arsenide alloys is indicated significantly higher than in gallium arsenide. A non-destructive etch-stain technique using an applied EMF produces excellent definition of p-n junctions and gallium layers. Efficiency of the same order as single gap cells has been achieved in one specie of variable gap cells. Spectral response data strongly supports the higher band gap "window" effect.

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